Reductive Nitrosylation of Tetraoxometallates. Part 14.[1] Generation and Proton Induced Disproportionation of the $Re(NO)^{3+}$ Moiety. Synthesis, Characterisation, and Electrochemistry of Novel Hydroxo- and Halogenonitrosyl Complexes of Rhenium

Ramgopal Bhattacharyya,* Partha S. Roy, and Anup K. Dasmahapatra
Department of Chemistry, Jadavpur University, Calcutta 700032, India

In an aqueous alkaline reaction medium, $[ReO_4]^-$ undergoes reductive nitrosylation by $NH_2OH{\cdot}HCl$ producing $[Re(NO)(OH)_4]^-$, isolated as APh_4(A = P or As) salts or as a neutral complex $[Re(NO)(OH)_3(L\text{–}L)]$ [L–L = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)]. The complexes show ν(NO) vibrations at *ca.* 1 680 cm^{-1} and their e.s.r. spectra suggest that, besides the hydroxo complex (C_{4v}), the L–L derivatives also possess axially symmetric structures. These complexes contain the $Re(NO)^{3+}$ [or $\{Re(NO)\}^5$] group and show spin-only magnetic moments and almost identical e.s.r. profiles in the polycrystalline condition, both at 298 and 77 K, showing $\langle g_{av}\rangle \approx 2.0$. A well defined sextet due to metal hyperfine structure is observed of which the two outermost peaks are further split to a triplet arising from ^{14}N (of NO) superhyperfine interaction. However, in frozen acetonitrile or dimethylformamide (dmf) the hyperfine structures collapse. These complexes of $Re(NO)^{3+}$ disproportionate when boiled with HX (X = Cl or Br but not I, which forms only $[ReI_6]^{3-}$ species), producing $[Re(NO)X_5]^-$ or $[Re(NO)X_4(phen)]$ [*i.e.* $Re(NO)^{4+}$], $[Re(NO)_2X_4]^-$ [*i.e.* $Re(NO)_2{}^{3+}$], and $[Re_2X_8]^{4-}$ ($Re_2{}^{4+}$). While a square-pyramidal structure (C_{4v}) can be suggested for the mononitrosyl halogeno complex anions from i.r. and electronic absorption spectra, these do not distinguish between axial–equatorial (C_s) or equatorial–equatorial (C_{2v}) dispositions of the two nitrosyl ligands in the dinitrosyl complexes. The seven-co-ordinate complexes $[Re(NO)X_4(phen)]$ undergo thermal and electrochemical (irreversible) reduction corresponding to two one-electron steps. The six-co-ordinate $Re(NO)^{4+}$ species, $[Re(NO)Cl_5]^-$, shows a similar electrochemical reduction process but the five-co-ordinate $[Re(NO)(OH)_4]^-$ is electro-inactive. The cyclic voltammogram of the $Re(NO)_2{}^{3+}$ species, $[Re(NO)_2Cl_4]^-$, reveals a reversible, $Re(NO)_2{}^{3+}$–$Re(NO)_2{}^{2+}$ couple at a formal potential of −0.04 V *vs.* a saturated calomel electrode {−0.42 V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$}.

The reductive nitrosylation of tetraoxometallates, *viz.* $[MO_4]^{n-}$ (M = Cr or Mo, *n* = 2; M = V, *n* = 3; or M = Os, *n* = 0) and subsequent isolation of pure metal nitrosyl derivatives[1–5] has so far been shown to occur only when another reducing agent, for instance, CN^-, NCS^-, $N_3{}^-$, or $C_2O_4{}^{2-}$ is used in the reaction medium along with NH_2OH, a reductant as well as a source of NO. It has been observed that $ReO_4{}^-$ as a substrate also responds[6] to the conventional 'twin-reagents' for the above reaction, producing $Re(NO)^{2+}$ [*i.e.* $\{Re(NO)\}^6$[†]] or $Re(NO)_2{}^{2+}$ [*i.e.* $\{Re(NO)_2\}^7$], a combination of reagents[6b] being necessary for the latter. However, NH_2OH alone has never been shown to act simultaneously as a combined multiple-electron reductant and nitrosylating agent on tetraoxometallates of other higher valent metal ions as substrates, in order to furnish clear cut metal nitrosyl derivatives.

Herein we report, for the first time, that alkaline NH_2OH reacts with $[ReO_4]^-$ to afford hitherto unknown rhenium nitrosyl complexes $\{[Re(NO)(OH)_4]^-$ or $[Re(NO)(OH)_3(L\text{–}L)]\}$ containing the $Re(NO)^{3+}$ moiety in a single-step process. The hydroxo derivatives are convenient precursors for a number of $Re(NO)^{4+}\{[Re(NO)X_5]^-$ or $[Re(NO)X_4(L\text{–}L)]\}$ and $Re(NO)_2{}^{3+}$ $\{[Re(NO)_2X_4]^-$ (X = Cl or Br)$\}$ complexes, and, in solution only, the species $[Re_2X_8]^{4-}$. It may be acclaimed that the multiple metal–metal bonded species $[Re_2X_8]^{4-}$ has for the first time been obtained using a starting material which does not contain any metal–metal bond, and, that it has also been achieved by chemical reduction of $[ReO_4]^-$ in a two-step process.

Results and Discussion

(*a*) *Overall Reaction Pattern.*—(*i*) *Generation of* $Re(NO)^{3+}$ *moiety.* Aqueous $K[ReO_4]$ reacts with alkaline $NH_2OH{\cdot}HCl$ to yield a red solution (**A**), which when treated with $[APh_4]Cl$, gives $[APh_4][Re(NO)(OH)_4]$ (**1**) [A = P (**1a**) or As (**1b**)], and with L–L affords $[Re(NO)(OH)_3(L\text{–}L)]$ (**2**) [L–L = 1,10-phenanthroline(phen) (**2a**) or 2,2′-bipyridine (bipy) (**2b**)]. The products, possessing the $Re(NO)^{3+}$ moiety, could not be obtained[5,6a] *via* the reductive nitrosylation pathway using the 'twin-reagents' mentioned above. It is noteworthy that the existence of some other derivatives containing the $Re(NO)^{3+}$ moiety has been reported by several groups of workers, who treated low-valent rhenium compounds (*viz.* cyano, chloro, carbonyl, or substituted phosphine complexes) with gaseous NO[7] or NOX (X = Cl or Br)[8] or concentrated HNO_3.[9] So, in most of the above cases the reaction can be classed as simple nitrosylation rather than reductive nitrosylation.

(*ii*) *Reactivity of the complexes containing* $Re(NO)^{3+}$. Interestingly, when solution (**A**) or compound (**1**) is boiled with concentrated solutions of HCl or HBr, the parent [initial in the case of (**1**)] solutions suffer a sharp colour change (see Experimental section) and from the resulting solution, in each case, judicious employment of counter ions ($[APh_4]^+$ or $[NBu^n{}_4]^+$) or L–L (phen or bipy) gives two different species, one containing a mono- and the other a di-nitrosyl–rhenium

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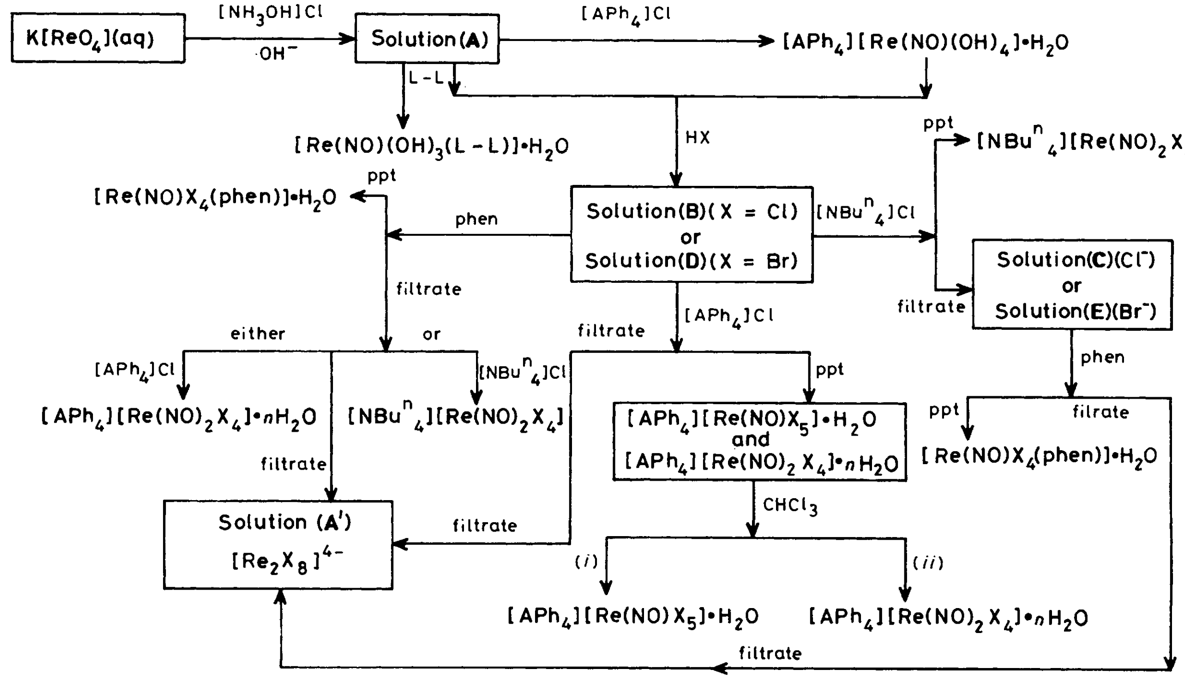
[†] The numerical superscripts indicate the total number of valence electrons in the metal and NO orbitals (see, for example, ref. 15).



Scheme 1. L–L = phen or bipy, A = P or As; X = Cl or Br ; (*i*) residue dissolved in CH_3CN and diethyl ether added; (*ii*) solution evaporated; ppt = precipitate; for value of *n* see Experimental section

moiety (see Scheme 1). These can be isolated in roughly 1:1 molar ratio, leaving behind a lemon-green (Cl) or reddish (Br) solution (**A**′). Infrared scanning of the solution in either case shows that apart from a very small concentration of the above nitrosyl products (which obviously have a marginal solubility), the bulk is a non-nitrosyl compound which does not contain any oxorhenium moiety but does contain Re–X bonds. The substance can neither be precipitated with bulky cations or anions, nor does it form any isolable derivative with L–L. The product may be $[Re_2X_8]^{4-}$, first suggested by Cotton *et al.*[10] who obtained it by polarographic reduction of $[Re_2X_8]^{2-}$, stepwise *via* $[Re_2X_8]^{3-}$. It could not be isolated or properly characterised by the earlier workers[10,11] who remarked that the species was unstable and underwent easy aerial oxidation to $[Re_2X_8]^{3-}$. On keeping (**A**′) in air a sharp and strong electronic spectral band at *ca.* 1 400 nm was observed, typical $[A_{2u}(\delta\pi) \longrightarrow B_{1u}(\delta^*)^{10}]$ of $[Re_2X_8]^{3-}$. Also, the species is e.s.r. active. The *X*-band e.s.r. spectrum in CH_2Cl_2 (water was distilled out at a reduced pressure and the residue taken up in CH_2Cl_2) shows [Figure 1(*a*)] that each main peak of the well defined sextet due to rhenium (^{185}Re and ^{187}Re, both with $I = \frac{5}{2}$) hyperfine structure[12a] is again split into a quartet due to interaction of the unpaired electron with ^{35}Cl and ^{37}Cl (both with $I = \frac{3}{2}$); *g* (solution) = 2.00, $\langle A\rangle_{Re}$ *ca.* 300—550 G, and $\langle A\rangle_{Cl}$ *ca.* 60—100 G.

Having established the composition of the non-nitrosyl compound a reaction scheme, as shown in equation (i) (A = P or As), can be drawn up to describe the proton induced disproportionation reaction of the $\{Re(NO)\}^5$ [*i.e.* $Re(NO)^{3+}$] moiety in HX (X = Cl or Br). Thus, this reaction is essentially an electrophilic attack by H^+ (assisted by X^-) on $\{Re(NO)\}^5$ which becomes facile only when strong HX solutions are used.

$$6[APh_4][Re(NO)(OH)_4] + 24HX + 2[APh_4]X \longrightarrow 2[APh_4][Re(NO)X_5] + 2[APh_4][Re(NO)_2X_4] + [APh_4]_4[Re_2X_8] + 24H_2O \quad (i)$$

We have previously[13] shown that rupture of a M–NO bond [in a $Mo(NO)^{3+}$ system] creates a M≡M bond. Conversely, creation of M–NO bonds by introducing NO groups into metal clusters ruptures metal–metal bonds.[14]

Nucleophiles such as AR_3 (A = P or As, R = alkyl or aryl), pyridine, SR_2, CN^-, NCS^-, or X^- have no apparent effect on the $\{Re(NO)\}^5$ moiety and the compounds can be crystallised unchanged from solutions containing these species, although OH^- causes oxidative cleavage of the Re–NO bonds. This experimental evidence supports nitrosyl–metal bonding *via* the NO^+ mode[15a,16] in the rhenium–nitrosyl systems. However, reversible nitrosyl–nitro conversion[16] which operates in ruthenium and some iron nitrosyl species does not take place here.

The parent hydroxo-species when boiled even with freshly prepared HI does not give any nitrosyl product. A hitherto unknown iodo-complex, $[ReI_6]^{3-}$, is the only species that can be isolated.

(*b*) *Complexes containing the* $Re(NO)^{3+}$ *Moiety*.—(*i*) *General characterisation, i.r. data, and structure.* Complexes of type (**1**) are 1:1 electrolytes in acetonitrile while those of (**2**) are monomeric and non-electrolytes in dimethylformamide (dmf) (Table 1). One water molecule in each case is only very loosely held in the lattice since it is lost below 100 °C [thermogravimetric (t.g.) and differential thermal analysis (d.t.)] and the process is weakly exothermic (d.t.). The hydroxo ligands and lattice-held water molecule together show a single and slightly broad ν(OH) i.r. band at *ca.* 3 400 cm⁻¹ but the $\delta(H_2O)$ band is apparently occluded in the low-energy tail of the ν(NO) vibrational band. The ν(NO) band, however, appears in the same region as observed in $Re(NO)^{2+}$ systems containing NCS^- or N_3^- ligands.[6a] The apparent constancy of ν(NO) for the complexes containing different ligand sets and different formal oxidation states for Re may be due to the combined effect of the variation of field factors between the *N*-bonded NCS^- or N_3^- and the hydroxo-ligands and the different co-ordination geometries existing in the two different systems. In the five-

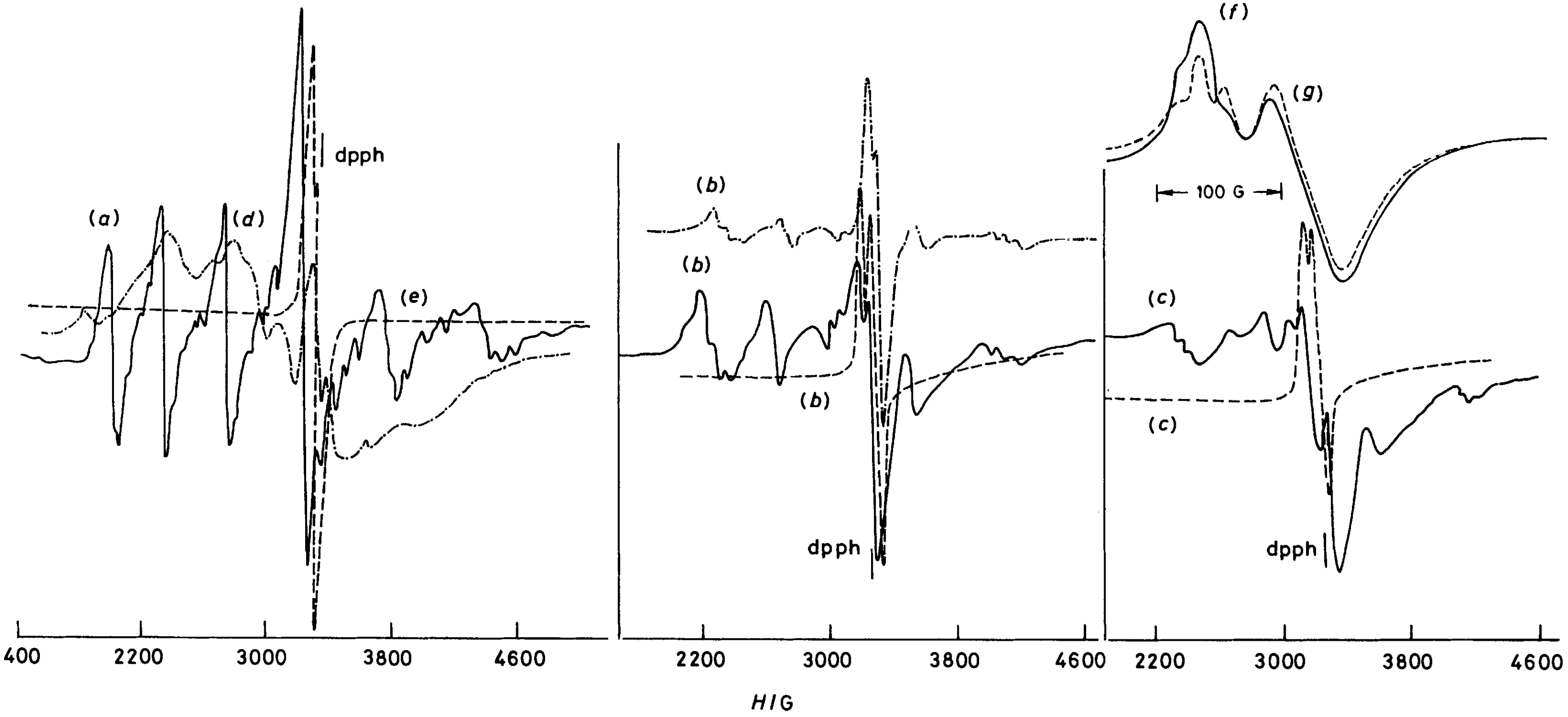


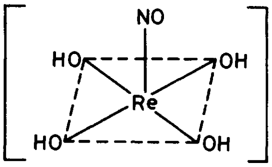
Figure 1. *X*-Band e.s.r. spectra of: (*a*) $[PPh_4]_3[Re_2Cl_8]$ in CH_2Cl_2 at 298 K (—); (*b*) $[AsPh_4][Re(NO)(OH)_4]\cdot H_2O$, polycrystalline, 298 K (—), 77 K (—·—·—), frozen acetonitrile (– – –); (*c*) $[Re(NO)(OH)_3(phen)]\cdot H_2O$, polycrystalline, 298 K (—), frozen dmf (– – –); (*d*) the product, $[Re(NO)Br_3(phen)]$, obtained by thermal reduction of (**7b**), 298 K (—·—·—); (*e*) the compound obtained after coulometric reduction of $[PPh_4][Re(NO)_2Cl_4]\cdot 1.5H_2O$ in frozen acetonitrile (– – –); (*f*) (*e*) at a better resolution (scan range 1 000 G, as against 8 000 G, in all the above cases), in frozen acetonitrile (—); and (*g*) $[Re(NO)_2(NCS)_2(phen)]^{6b}$ in frozen acetonitrile (– – –), quality of resolution as in (*f*)

Table 1. Analytical[a] and physical data of the complexes

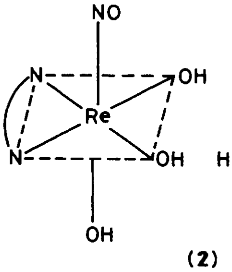
	Complex	Analysis (%) C	H	N	X	Selected i.r. data (cm^{-1}) ν(NO)	ν(Re–N)(due to Re–NO)	ν(Re–X)	Λ_M/Ω^{-1} cm^2 mol^{-1}
(1a)	$[PPh_4][Re(NO)(OH)_4]\cdot H_2O$[b]	44.5 (44.9)	4.4 (4.1)	1.9 (2.2)	—	1 685s	610s	—	135[c]
(1b)	$[AsPh_4][Re(NO)(OH)_4]\cdot H_2O$	41.7 (42.0)	4.1 (3.8)	1.8 (2.0)	—	1 685s	610w	—	125[c]
(2a)	$[Re(NO)(OH)_3(phen)]\cdot H_2O$[d]	30.7 (31.0)	3.2 (2.8)	8.6 (9.0)	—	1 680s	610w	—	e,f
(2b)	$[Re(NO)(OH)_3(bipy)]\cdot H_2O$[d]	22.4 (22.7)	3.5 (3.1)	9.7 (10.0)	—	1 680s	610w	—	e,f
(3a)	$[PPh_4][Re(NO)Cl_5]\cdot H_2O$[b]	37.9 (38.3)	3.2 (2.9)	1.6 (1.9)	23.1 (23.6)	1 730s	590w	330m, 315m, 252m	120[c]
(3b)	$[AsPh_4][Re(NO)Cl_5]\cdot H_2O$	35.9 (36.2)	2.5 (2.8)	1.8 (1.8)	21.9 (22.3)	1 740s,[g] 1 750s[g]	565w	340m, 300m, 238m	130[c]
(4a)	$[PPh_4][Re(NO)Br_5]\cdot H_2O$[b]	29.3 (29.6)	2.5 (2.3)	1.2 (1.4)	40.5 (41.1)	1 740s	590w	225m, 155 (sh)	125[c]
(4b)	$[AsPh_4][Re(NO)Br_5]\cdot H_2O$	28.0 (28.3)	2.3 (2.2)	1.6 (1.4)	39.7 (39.3)	1 740s	595w	205m, 160m	130[c]
(5a)	$[PPh_4][Re(NO)_2Cl_4]\cdot 1.5H_2O$[b]	38.0 (38.2)	3.3 (3.0)	3.4 (3.7)	18.5 (18.8)	1 865s, 1 750s	600w, 580w	348m, 310m, 275w, 220m	125[c]
(5b)	$[AsPh_4][Re(NO)_2Cl_4]\cdot H_2O$	36.1 (36.5)	3.1 (2.8)	3.3 (3.6)	17.6 (18.0)	1 870s, 1 762s	560w,[g] 550w[g]	340m, 305m, 275m, 225m	120[c]
(5c)	$[NBu^n_4][Re(NO)_2Cl_4]$	30.1 (30.5)	6.0 (5.7)	6.4 (6.7)	22.5 (22.5)	1 870s, 1 775s	600w, 570w	340m, 308m, 278m, 220m	140[c]
(6a)	$[PPh_4][Re(NO)_2Br_4]\cdot H_2O$[b]	30.8 (31.2)	2.6 (2.4)	2.9 (3.0)	34.1 (34.6)	1 860s, 1 750s	610w, 580w	218m, 204m, 182m, 155m	120[c]
(6b)	$[AsPh_4][Re(NO)_2Br_4]\cdot H_2O$	29.2 (29.8)	2.5 (2.3)	2.5 (2.9)	33.6 (33.1)	1 860s, 1 740s	590w	245m, 215m, 180m, 160m	135[c]
(6c)	$[NBu^n_4][Re(NO)_2Br_4]$	22.9 (23.2)	4.9 (4.6)	4.8 (5.1)	38.3 (38.7)	1 865s, 1 780s	610w, 590w	222m, 200m, 168m, 155m	135[c]
(7a)	$[Re(NO)Cl_4(phen)]\cdot H_2O$[d]	25.5 (25.9)	2.2 (1.8)	7.3 (7.6)	25.0 (25.5)	1 740s,[g] 1 770s[g]	615w	305m, 275m, 245m, 220m	8[e]
(7b)	$[Re(NO)Br_4(phen)]\cdot H_2O$[d]	19.2 (18.6)	1.7 (1.4)	5.4 (5.7)	45.3 (45.6)	1 733s,[g] 1 762s[g]	615w	227m, 205m, 178m, 162m	10[e]

[a] Calculated values in parentheses. [b] %P = 4.7 (4.9) (**1a**); 3.8 (4.1) (**3a**); 4.0 (4.2) (**4a**); 4.0 (4.2) (**5a**), and 3.2 (3.4) (**6a**) respectively. [c] In acetonitrile. [d] ν(Re–N) due to (L–L); 450s (**2a**), 450w (**2b**), 450w[g], 435w[g] (**7a**), and 450w (**7b**). [e] In dmf. [f] Non-electrolyte. [g] The pair comprises a single split band.

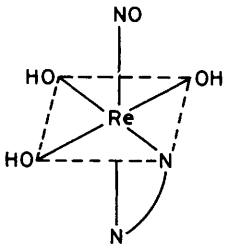
co-ordinate NCS$^-$ and N$_3$$^-$ cases [Re(NO)$^{2+}$] trigonal-bipyramidal (tbp) geometry was assumed, backed by spectroscopic evidence,[6a] but in the present case [Re(NO)$^{3+}$] square-pyramidal (sp) geometry with axial NO [(**1**) and (**2**)] conforms to the chemical and spectroscopic data. However, compared with the cyano-complexes of the Re(NO)$^{2+}$ series, where ν(NO) is found at 1 650 cm^{-1} it appears that its position in the present Re(NO)$^{3+}$ system is in the right region. Compounds (**2**) can have two possible isomeric structures, (**I**) and (**II**), depending on whether two L–L nitrogens are in equatorial–equatorial (ee) or axial–equatorial (ae) dispositions. The compounds isolated possess structure (**I**) as inferred from e.s.r. and visible spectra (see below).



(**1**)



(**I**)



(**II**)

(**2**)

(*ii*) *Magnetic properties and e.s.r. spectra.* The five-co-ordinate complex (**1**) is assumed to have C_{4v} symmetry and hence an (e^4) ($b_2{}^1$) ground-state configuration.[15a] The lower symmetry six-co-ordinate complex (**2a**) can be described by the same m.o. energy levels.[15a] Both (**1**) and (**2**) have $\mu_{eff.}$ values of *ca.* 1.8. Only a slight increase of the $\mu_{eff.}$ from the spin-only value owing to the negative (low-spin d^5) value of the spin–orbit coupling constant is due to the orbital non-degeneracy of the singly occupied molecular orbital (s.o.m.o.) involved. Also, the *X*-band e.s.r. profiles [Figure 1(*b*) and (*c*)] of both (**1**) and (**2**) in their polycrystalline state are almost identical at 298 and 77 K. The signals exhibit axial symmetry but have complex hyperfine splitting (Table 2). Complex (**2**) also exhibits an axially symmetric e.s.r. spectrum, indicating that its structure should be represented by (**I**). Although both (**I**) and (**II**) have almost the same symmetry status, the effective symmetry (metal–donor

Table 2. E.s.r. parameters of complexes containing the $\{Re(NO)\}^5$ moiety

Complex[a]	Temp (K)	g_s[b]	$g_{\parallel}$[c]	$g_{\perp}$[c]	$g_{av.}$[d]	$\langle A \rangle_{Re}$/G[e]	$\langle A \rangle_{NO}$/G
(1b)[f]	298	2.00	1.97	2.07	2.04	350—630	50—70
(1b)[f]	77	2.02	1.99	2.05	2.03	350—640	60—80
(1b)[g]	77	1.99	1.98	2.04	2.02	—	—
(2a)[f]	298	2.00	1.96	2.11	2.06	210—580	70—80
(2a)[h]	77	2.00	1.98	2.03	2.01	—	—
(8)[i]	298	1.98	1.91	2.01	1.97	200—620	—

[a] The spectra of the $[APh_4]^+$ (A = P or As) analogues are virtually identical. [b] g_s represents the g value of the derivative curve in the polycrystalline or solution phase as indicated. [c] For spin paired d^5 systems $g_{\perp} > 2$ and $g_{\parallel} < 2$; see ref. 12(*a*). [d] $g_{av.} = (2g_{\perp} + g_{\parallel})/3$. [e] The available data so far obtained do not permit an unequivocal assessment of $\langle A_{\parallel} \rangle_{Re}$, $\langle A_{\perp} \rangle_{Re}$, and $\langle A_0 \rangle_{Re}$. [f] In polycrystalline sample. [g] In frozen acetonitrile. [h] In frozen dmf. [i] Thermolysis intermediate from the corresponding tetrabromo product.

Table 3. Electronic spectral data

Complex	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
(1a)[a]	628 (250), 408 (865), 340 (225)
(1b)[a]	628 (255), 408 (970), 320 (265)
(2a)[b]	408 (440), 288 (1 380)
(2b)[b]	400 (425), 310 (1 160))
(3a)[a]	520 (52), 428 (250), 368 (2 125), 300 (1 625)
(3b)[a]	520 (54), 428 (289), 368 (2 174), 292 (1 740)
(4a)[a]	540 (58), 428 (609), 374 (2 073), 308 (487)
(4b)[a]	528 (55), 420 (604), 376 (2 014), 308 (402)
(5a)[a]	612 (78), 450 (435), 360 (120), 320 (195)
(5b)[a]	620 (100), 420 (520), 320 (125), 308 (145)
(5c)[a]	612 (55), 450 (378), 360 (186), 320 (430)
(6a)[a]	640 (24), 470 (463), 420 (720), 376 (515)
(6b)[a]	640 (20), 474 (427), 412 (787), 376 (560)
(6c)[a]	648 (15), 476 (472), 420 (650), 376 (472)
(7a)[b]	510 (140), 364 (2 757)
(7b)[b]	520 (154), 384 (2 550)

[a] In acetonitrile. [b] In dmf. Intraligand transitions are not listed.

atom chromophore) in (**I**) should be higher than the strict symmetry. Thus, the assigned structure (**I**) is more in conformity with the e.s.r. data. A well defined sextet is observed which arises from hyperfine coupling with the spin-active ^{185}Re and ^{187}Re nuclei [both have $I = \frac{5}{2}$, see ref. 12(*a*)]. However, the two outermost peaks and an inner peak, close to the derivative curve, undergo further splitting into triplets due to interaction of the unpaired electron with ^{14}N of NO[12*b*,17] [Figure 1(*b*) and (*c*)]. However, since the unpaired electron in both the five- and six-co-ordinate cases occupies a $b_2(xy)$ orbital which is non-bonding with respect to the NO group, the observation of ^{14}N hyperfine (in fact superhyperfine) coupling necessitates invoking spin polarisation of the e orbital (d_{xz}, d_{yz}) with an admixture of NO π and π^* orbitals.[12*b*,15*a*,17] Interestingly enough, the hyperfine structure vanishes when the spectra are taken, even in frozen acetonitrile [(**1**)] or dmf [(**2**)], and consequently the features of g-tensor anisotropy sharpen up [Figure 1(*b*) and (*c*)].

(*iii*) *Electronic spectral data.* The strict symmetry of (**2**) is much lower than that of (**1**) (C_{4v}). However, the effective symmetry may not be vastly different from C_{4v} and hence the energy levels of (**I**) may not differ substantially from those of the C_{4v} case. The three electronic absorption bands in (**1**) (five-co-ordinate) may be designated as $b_2 \longrightarrow e$, $b_2 \longrightarrow a_1$, and $b_2 \longrightarrow b_1$.[15*a*] In (**I**) (six-co-ordinate), however, only two bands with enhanced intensities appear in dmf solution, in both (**2a**) and (**2b**) (Table 3). These may correspond to $b_2 \longrightarrow e$ (the e level[15*a*] is not split in a symmetry lower than C_{4v} or a low-energy transition would have been observed) and $b_2 \longrightarrow b_1$ transitions, the high-energy $b_2 \longrightarrow a_1$ transition being missing. The energy difference between the ground and excited levels in the six-co-ordinate systems is greater than that in the five-co-ordinate one (see Table 3) and the high-energy transition in the case of the former will be embedded within the intraligand (phen or bipy) transitions. These observations lend further support towards the structures (**1**) and (**I**) predicted on the basis of i.r. and e.s.r. data.

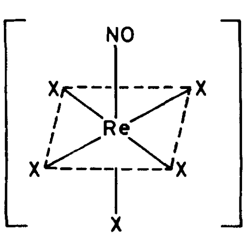
(*c*) *Complexes containing* $Re(NO)^{4+}$ *and* $Re(NO)_2{}^{3+}$ *Moieties*.—(*i*) *Synthesis.* As shown in Scheme 1, Re^{II} (based on NO^+ formalism) undergoes disproportionation on reaction with HCl or HBr to give mono- and di-nitrosyl halogenorhenates where the metal ion exists in the +3 and +1 oxidation states respectively. The $[APh_4]^+$ ion precipitates both species from which mono- and di-nitrosyls, *viz.* $[APh_4][Re(NO)X_5]$ [X = Cl, A = P (**3a**) or As (**3b**); X = Br, A = P (**4a**) or As (**4b**)] and $[APh_4][Re(NO)_2X_4]$ [X = Cl, A = P (**5a**) or As (**5b**); X = Br, A = P (**6a**) or As (**6b**)] can be separated by taking advantage of their solubility differences in organic solvents. However, $[NBu^n{}_4]^+$ precipitates only the dinitrosyl species, $[NBu^n{}_4][Re(NO)_2Cl_4]$ (**5c**) and $[NBu^n{}_4][Re(NO)_2Br_4]$ (**6c**). When (**5c**) and (**6c**) are removed by filtration, the mononitrosyl species $[Re(NO)X_4(phen)]$[X = Cl (**7a**) or Br (**7b**)] can be precipitated from solution by addition of phen. 1,10-Phenanthroline precipitates only the mononitrosyl species and not the dinitrosyl from a solution containing both. However, if (**5c**) and (**6c**) are filtered out, (**3a**), (**3b**), (**4a**), and (**4b**) cannot be precipitated from the filtrate by addition of $[APh_4]Cl$. That the mono- and di-nitrosyl products are formed in 1:1 molar ratio is demonstrated by the simultaneous isolation of mono- and di-nitrosyls by addition of $[APh_4]^+$. But, when the preferential precipitation of mono- or di-nitrosyl species occurred as a result of addition of phen or $[NBu^n{}_4]^+$, respectively, then the relative yield of the species precipitated out first becomes greater than that separated out later due to the occurrence of a mononitrosyl–dinitrosyl equilibrium, as shown in equation (ii).

$$[Re(NO)X_5]^- + NO \rightleftharpoons [Re(NO)_2X_4]^- + X^- \quad \text{(ii)}$$

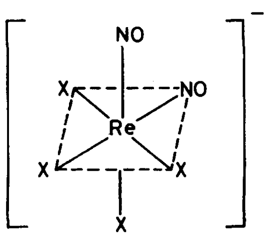
(*ii*) *General characterisation, i.r. data, and structural aspects.* Compounds (**3**)—(**6**) are 1:1 electrolytes in acetonitrile (Table 1) and both (**7a**) and (**7b**) are practically non-electrolytes in dmf showing only a marginal dissociation of X^-. The mononitrosyl complexes exhibit a single ν(NO) vibrational band in the region *ca.* 1 740 cm^{-1} (Table 1), although in some cases [(**3b**) and (**7b**)] the band is split (separation 10 and 29 cm^{-1} respectively), which may be due to the solid-state effect. The splitting of ν(NO) in mononitrosyl halogenometallates has been ascribed[18] to a large change in the bond dipole moment of the NO group during its vibration and hence a sensitivity to the external electric field. The position of ν(NO) in these $Re(NO)^{4+}$ species is, as expected, *ca.* 50 cm^{-1} higher than in the corresponding tripositive species. The oxidation state of rhenium in the former is one unit higher (*i.e.* +3) than in the latter and there is a weaker M $\longrightarrow$ NO π back-donation. The dinitrosyl complexes containing $Re(NO)_2{}^{3+}$ species show two prominent ν(NO) vibrations (Table 1) situated with a splitting of 85—110 cm^{-1}, typical for a *cis*-dinitrosyl complex. The band positions (Table 1), are, as expected, at higher frequencies than those observed in the complexes containing the $Re(NO)_2{}^{2+}$ moiety.[6b]

Compounds (**3**)—(**6**) are six-co-ordinate while (**7**) are seven-co-ordinate. Again, assuming NO to be axial and M-N-O to be linear* (**3a**), (**3b**), (**4a**), and (**4b**) may have C_{4v} symmetry. Since the metal ion is expected to be raised out of the equatorial plane towards the nitrosyl ligand, the three ν(ReCl) i.r. bands in (**3a**) and (**3b**) (Table 1) may be assigned to $\nu_{asym.}(ReCl_4)$, $\nu_{sym.}(ReCl_4)$, and ν(ReCl) (*trans*), in order of decreasing wavenumbers.[20–22] However, in the corresponding bromo-complexes, (**4a**) and (**4b**), only two bands are observed and that around 160 cm^{-1} may be assigned to ν(ReBr)(*trans*) while $\nu(ReBr_4)$ appears as a single band at *ca.* 200 cm^{-1} (see Table 1), the symmetric and asymmetric vibrations being overlapped.[20–22] There is a rather strong cation dependence of the Re–Cl vibrations [(**3a**) and (**3b**) *cf.* (**4a**) and (**4b**)]. Complexes (**7a**) and (**7b**) have low symmetry and the observation of four ν(ReCl) vibrations (Table 1) is as expected. The observed data however are not sufficient to predict any structure for (**7a**) and (**7b**) since seven-co-ordinate species are capable of existing in three different stereochemical configurations.[23]

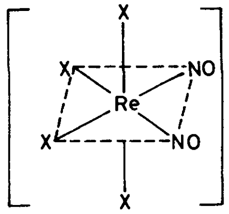
The dinitrosyl complexes should all exhibit C_s symmetry[15a] (since the NO groups are *cis*) with one NO axial and the other equatorial as is structurally characterized for a $\{M(NO)_2\}^6$ system.[24] The structures of the dinitrosyl compounds should be represented by (**IV**), although the possibility of (**V**) containing both NO groups in the equatorial positions and conforming to C_{2v} symmetry cannot be ruled out.[15a] Of course, in both symmetries, all four Re–X bonds should give rise to four i.r. active $\nu(ReX_4)$ vibrations. This, in fact, is the case (Table 1). However, i.r. data cannot distinguish between structures (**IV**) and (**V**).



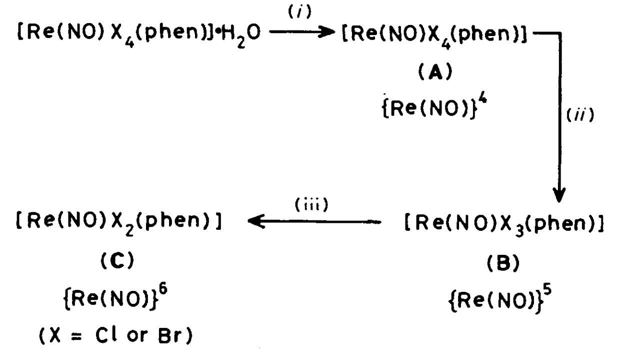
(**III**)
(**3**) (X = Cl)
(**4**) (X = Br)



(**IV**)
(**5**) (X = Cl)
(**6**) (X = Br)



(**V**)
(**5**) (X = Cl)
(**6**) (X = Br)



Scheme 2. (*i*) 50 °C (X = Cl), 80 °C (X = Br), $-H_2O$, endothermic; (*ii*) 200 °C, $-\frac{1}{2}X_2$, X = Cl, endothermic; X = Br, exothermic; (*iii*) 250 °C, $-\frac{1}{2}X_2$, X = Cl, endothermic; X = Br, exothermic. In both cases intermediate (**A**) exists in the temperature range 120—190, (**B**) in 240—260, and (**C**) in 340—410 °C

(*iii*) *Magnetic susceptibility and electronic spectra.* The C_{4v} species (**3**) and (**4**) containing the $\{Re(NO)\}^4$ moiety should have an $(e)^4$ ground state which conforms with their diamagnetism. Hence the four electronic spectral bands (Table 3) in each of the above complexes may be designated as $e \longrightarrow b_2$, $e \longrightarrow e$, $e \longrightarrow b_1$, and $e \longrightarrow a_1$ transitions.

The four electronic spectral bands observed in the $\{Re(NO)_2\}^6$ dinitrosyl complexes (Table 3), in acetonitrile, may be assigned to $a' \longrightarrow b_1$, $a' \longrightarrow a'$, $a' \longrightarrow a'$, and $a' \longrightarrow a''$ transitions if the two NO groups occupy axial–equatorial sites [*i.e.* C_s symmetry, structure (**IV**)]. However, when the alternative C_{2v} structure (**V**) is considered, the observed bands can be assigned as $b_2 \longrightarrow a_1$, $b_2 \longrightarrow b_1$, $b_2 \longrightarrow b_2$, and $b_2 \longrightarrow a_2$.[15a] In both models, a slight deviation is expected for the two nitrosyl groups from linearity.[15a] The electronic spectral data cannot therefore distinguish between the two structures and *X*-ray diffraction studies are necessary. The diamagnetism of the isolated dinitrosyl complexes is also consistent with the orbital scheme. In C_s and C_{2v} models the ground-state configurations are $(a'')^2\,(a')^2\,(a')^2$ and $(a_2)^2\,(a_1)^2\,(b_2)^2$ respectively. The neutral molecules (**7a**) and (**7b**) show only two electronic spectral bands in dmf solution. The absence of any molecular orbital scheme for seven-co-ordinate $\{M(NO)\}^n$ systems prevents the assignment of these bands.

(*iv*) *Thermoanalytical studies.* One water molecule (1.5 H_2O in (**5a**); excepting the $[NBu^n{}_4]^+$ salts) is held in the lattice, since it is lost at temperatures well below 100 °C. The thermal decomposition of $[Re(NO)X_4(phen)]$ (**7**) (X = Cl or Br) however in a dinitrogen atmosphere shows interesting results. The stepwise thermal reduction of the $\{Re(NO)\}^4$ moiety, which is obvious from their thermograms (t.g. and d.t.), is represented by Scheme 2.

The t.g. data agree fairly well with the percentage weight loss expected (calc.) for the formation of intermediates (**A**), (**B**), and (**C**). Thereafter, a highly exothermic reaction occurs leading to the total decomposition of the molecules concerned. The endothermic loss of chlorine in (**7a**) as against the exothemicity of bromine loss in (**7b**) may be attributed to the higher ionic radius of Br$^-$ compared to Cl$^-$ and the consequent steric factor which, however, controls only the direction of the enthalpy change while the gross thermodynamic stability is of the same order, since the temperatures of the successive decompositions, *etc.*, are almost the same in both cases. As expected, intermediate (**B**) [*i.e.* compound (**8**)] is e.s.r. sensitive and the spectral features† [Figure 1(*d*)] are typical (Table 2) for the moiety

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* There is no exception to this behaviour in structurally confirmed cases containing $\{M(NO)\}^n$ moieties where n = 4—6.[19]

† Spectrum of the chloro complex is identical with the bromo analogue.

Table 4. Cyclic voltammetric data at 298 K for $[PPh_4][Re(NO)_2Cl_4]\cdot1.5H_2O$ in CH_3CN *vs.* s.c.e. {values *vs.* $[Fe(\eta\text{-}C_5H_5)_2]\text{-}[Fe(\eta\text{-}C_5H_5)_2]^+$ are shown in parentheses}

Scan rate ($mV\ s^{-1}$)	E_{pc}/V	E_{pa}/V	E^0_{298}/V*	$\Delta E_p/mV$	i_{pc}/i_{pa}
50	−0.08 (−0.46)	0.00 (−0.38)	−0.04 (−0.42)	80	0.94
100	−0.08 (−0.46)	0.00 (−0.38)	−0.04 (−0.42)	80	0.99
200	−0.08 (−0.46)	0.00 (−0.38)	−0.04 (−0.42)	80	0.95

* E^0_{298} = average of E_{pa} and E_{pc}.

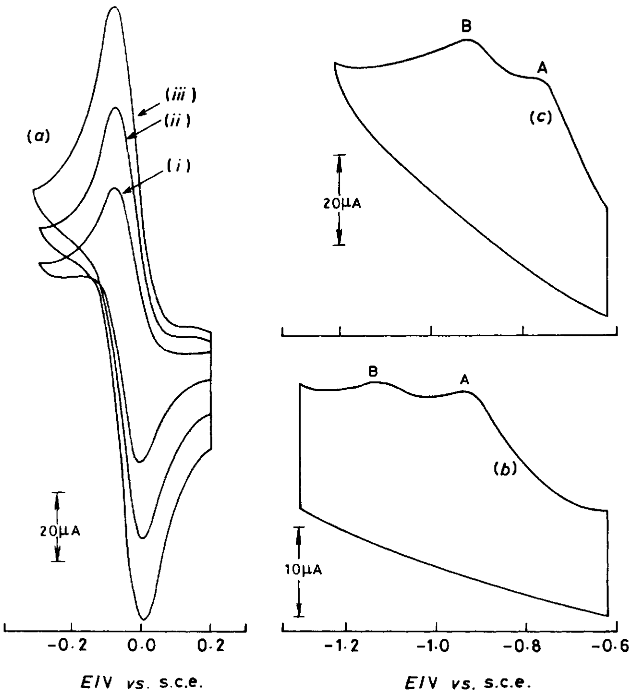

Figure 2. Segmented cyclic voltammograms of (*a*) $[PPh_4][Re(NO)_2Cl_4]\cdot1.5H_2O$ in acetonitrile at scan rates (*i*) 50, (*ii*) 100, and (*iii*) 200 $mV\ s^{-1}$, (*b*) $[Re(NO)Br_4(phen)]\cdot H_2O$ in dmf (scan rate 50 $mV\ s^{-1}$) and (*c*) $[PPh_4][Re(NO)Cl_5]\cdot H_2O$ in acetonitrile (scan rate 50 $mV\ s^{-1}$). All in 0.1 mol dm^{-3} $[NEt_4]ClO_4$ at a platinum electrode

($\{ReNO\}^5$) they represent. The rhenium hyperfine sextet is also observed here in the polycrystalline state, but the possible triplets due to superhyperfine splitting of ^{14}N of NO are not resolved here. The product (**C**) is diamagnetic like (**A**). These magnetic properties of the intermediates actually confirm the modes of thermal decomposition suggested (Scheme 2). While the original complexes (**7**) containing rhenium in the formally +3 oxidation state show a split ν(NO) band (Table 1), intermediates (**B**) (Re, +2) and (**C**) (Re, +1) show a single band each (occurring in the same region for X = Cl and Br), the former at 1 765 and the latter at 1 760 cm^{-1}. The apparent constancy of the ν(NO) band even after progressive reduction at the metal centre may be attributed to two opposing effects: (1) reduction from $\{Re(NO)\}^4$ to $\{Re(NO)\}^5$ and finally to $\{Re(NO)\}^6$ necessitates a facilitated Re ⟶ NO back-bonding as we go from left to right, predicting a lowering in the ν(NO) frequencies, and (2) successive lowering of the metal co-ordination number concomitant to reduction lowers the accumulation of electronic charge density over rhenium, thereby hindering the same back-donation and hence increasing the ν(NO) frequencies. The net effect (as is also observed) is a slight change or no change at all in the said frequencies.

(*v*) *Electrochemistry of complexes containing generated* $Re(NO)^{3+}$, $Re(NO)^{4+}$, *and* $Re(NO)_2{}^{3+}$ *moieties.* Voltammetry was carried out in acetonitrile [(**7b**) in dmf] solutions at a platinum working electrode. All potentials are referenced to the saturated calomel electrode (s.c.e.). Tetraethylammonium perchlorate was used as an inert electrolyte in each case. The formal potentials are also expressed (in parentheses in the relevant table) relative to E^0_{298} of the $[Fe(\eta\text{-}C_5H_5)_2]\text{-}[Fe(\eta\text{-}C_5H_5)_2]^+$ couple *vs.* s.c.e., separately measured under identical experimental conditions, solvents, and inert electrolytes as used for the measurements of unknown solutions. That ferrocene[25] can be used as an internal standard in electrochemical measurements is possibly valid only in the cases of less reactive compounds preferably involving common and chemically stable metal valence states. In the presence of our nitrosyl compounds the formal potential of the $[Fe(\eta\text{-}C_5H_5)_2]\text{-}[Fe(\eta\text{-}C_5H_5)_2]^+$ couple itself changes in both acetonitrile and dmf solvents compared to the value observed in the absence of the particular compound, even though the systems do not possess overlapping waves. Moreover, the claim of Strehlow and co-workers[26] that this couple behaves as a solvent independent redox couple seems to be questionable; $E^\ominus$, E_{pa}, E_{pc}, and ΔE_p of the latter all significantly differ in dmf from those measured in CH_3CN.

Both the $[PPh_4]^+$ and $[AsPh_4]^+$ salts of the complex anion containing the $Re(NO)^{3+}$ moiety do not show clear oxidative or reductive processes in the range −1.8 to +1.8 V *vs.* s.c.e. However, $[PPh_4][Re(NO)_2Cl_4]\cdot1.5H_2O$ (**5a**) displays a nearly reversible cyclic response [Figure 2(*a*)] at a potential around 0.00 V {−0.38 V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]\text{-}[Fe(\eta\text{-}C_5H_5)_2]^+$ couple} assigned to the electrode process represented in equation (iii). Details of the voltammetric parameters are given in Table 4. Exhaustive electrolysis (coulometry) at more negative potentials than −0.3 V (−0.30 V *vs.* s.c.e.) gives a coulomb count which corresponds to one electron change. The colour of the solution changes from yellowish green to pale yellow after

$$Re(NO)_2{}^{3+} + e^- \rightleftharpoons Re(NO)_2{}^{2+} \qquad \text{(iii)}$$

reduction. Since the product moiety should have an electronic configuration $\{Re(NO)_2\}^7$, an e.s.r. spectrum of the reduced solution (frozen at 77 K) was recorded and is shown in Figure 1(*e*). The e.s.r. parameters, $\langle g_s \rangle$, $\langle g_\perp \rangle$, $\langle g_\parallel \rangle$, and $\langle g_{av} \rangle$ are 1.99, 2.04, 1.97, and 2.02 respectively and compare well with those of other six-co-ordinate complexes having the $\{Re(NO)_2\}^7$ moiety.[6b] However, the hyperfine structure (metal or NO) observed in the latter case, in polycrystalline condition, is absent here. Such is also the profile of the e.s.r. spectrum of the authentic $\{Re(NO)_2\}^7$ complex, $[Re(NO)_2(NCS)_2(phen)]$,[6b] in frozen acetonitrile solution when measured using a large scan range as in Figure 1(*e*) but at a better resolution (scan range 1 000 G), also both the spectra (authentic and electro-reduced) are essentially identical [see Figure 1(*f*) and (*g*)]. Rhenium hyperfine structure vanishes and rather broad (features being a little sharper in the case of the thiocyanato complex) ^{14}N (of NO) hyperfine structure (*ca.* 50 G) appears, and that too, only in the perpendicular region. In the present case the logical conclusion, based on the m.o. diagram of $\{M(NO)_2\}^7$,[15b] is that in the solution phase, the s.o.m.o. is based only on nitrosyl orbitals [as also inferred in the case of $\{Mo(NO)_2\}^7$ species obtained by electrochemical reduction],[27] while the solid-phase spectrum shows the nature of the s.o.m.o. to be an admixture of metal *d* and π^*NO character. However, the general situation is not so simple, since a more complex reason seems to operate in the cases of collapse of both metal and ^{14}N hyperfines in $\{Re(NO)\}^5$ species in solution phase (even at a high resolution) as against both being observed (metal hyperfines being more prominent) in the solid state (see above), insofar as the s.o.m.o. involved here is of predominantly metal *d* character.

The $Re(NO)^{4+}$ moieties in $[PPh_4][Re(NO)Cl_5]$ (**3a**) and $[Re(NO)Br_4(phen)]$ (**7b**) show almost identical electroactivity. Complex (**3a**) shows two irreversible reduction peaks at -0.76 and -0.92 V in acetonitrile solution *vs.* s.c.e. (-1.24 and -1.42 V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$) whilst the bromo derivative exhibits peaks at -0.94 and -1.12 V respectively in dmf *vs.* s.c.e. (-1.39 and -1.67 V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$(Fe(\eta\text{-}C_5H_5)_2]^+$ (Figure 2). These two irreversible reduction waves may represent the electrochemical reductions shown in equation (iv) in both cases. However, due to the closeness of the reduction waves A and B in both cases it is very difficult to carry out a coulometric reduction to prepare A free of B to characterise A. Since the complexes have different charges and co-ordination numbers and their electrochemistry is studied in different solvents, it is very difficult to comment on the relative size of the observed reductive potentials. However, the relatively easier reduction of (**3**) over (**7**) may be due to the achievement of an 18-electron configuration in the former case, *via* a 17-electron step [equation (v)].

$$Re(NO)^{4+} \xrightarrow{+e^-} Re(NO)^{3+} \xrightarrow{+e^-} Re(NO)^{2+} \qquad \text{(iv)}$$

$$[Re(NO)Cl_5]^- \xrightarrow{+e^-} [Re(NO)Cl_5]^{2-} \xrightarrow{+e^-} [Re(NO)Cl_5]^{3-} \qquad \text{(v)}$$

Experimental

Materials and Methods.—The starting material, $K[ReO_4]$, was of extra pure quality and obtained from Johnson Mathey. All reagents required for compound preparation were of analytical grade. The analytical grade solvents used for physicochemical studies were further purified by a literature method[28] before use. Water of high purity was obtained by distilling deionised water from $K[MnO_4]$. Sodium perchlorate for electrochemical work was recrystallised from water and the supporting electrolyte $[NEt_4]ClO_4$ was prepared using the literature method.[29] Dinitrogen was purified by bubbling it through an alkaline dithionite reducing solution. Benzil was further crystallised from ethanol. Chemically pure grade ferrocene (Sigma Chemical Company) was used directly. Infrared spectra of CsI pellets (4 000—200 cm^{-1}) were recorded on a model 597 Perkin-Elmer i.r. spectrophotometer, and those of polythene pellets (500—150 cm^{-1}) with a model 130. I.r. spectra of aqueous solutions (4 000—700 cm^{-1}) were measured using an Irtran 2 demountable cell with polytetrafluoroethylene spacers. Electronic spectra were recorded on a Pye-Unicam SP8-150 UV-VIS, or a Hitachi 330 UV-VIS-NIR spectrophotometer. All pH measurements were made with an E.C. (India) digital pH meter (model 5651). A Knauer vapour pressure osmometer was used for the molecular weight determination using benzil as calibrant and the solution conductances were measured with a Wayne Kerr B 331 autobalance precision bridge. Magnetic susceptibilities were obtained by the Guoy method with the help of a model 155 PAR vibrating sample magnetometer. *X*-Band e.s.r. spectra were obtained using a Varian E-109C spectrometer fitted with a quartz Dewar for measurement at 77 K. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) (g = 2.0037). Thermoanalyses were made on a DT 30 Shimadzu thermoanalyser. Voltammetric measurements were done using a model 370-4 PAR electrochemistry system [model 174A polarographic analyser, model 175 universal programmer, model RE0074 XY recorder, model 173 potentiostat, model 179 digital coulometer, and model 377A cell system]. All experiments were performed under a dinitrogen atmosphere in a three-electrode cell using a planar model 39273 Beckman platinum-inlay working electrode, a platinum wire auxiliary electrode, and saturated calomel reference electrode (s.c.e.). For coulometry a platinum-wire-gauze working electrode was used. All results were collected at 298 K and the reported potentials are uncorrected for junction contribution. Elemental analyses were performed in the Faculty of Chemistry, University of Bielefeld and in the Beller Laboratories, Göttingen, West Germany. Halogen contents were estimated as silver halides using a standard method.[30]

Preparation of the Complexes.—*Preparation of solution* (**A**). A mixture of $K[ReO_4]$ (0.11 g, 0.35 mmol) and $NH_2OH \cdot HCl$ (0.36 g, 5.25 mmol) was dissolved in water (25 cm^3). The resulting solution was heated to *ca.* 80 °C for 10 min with constant stirring. Solid NaOH beads were gradually added to the stirred solution until it turned red and the pH increased to *ca.* 9.5. The red solution was again stirred at 80 °C for 15 min and then cooled to room temperature.

$[APh_4][Re(NO)(OH)_4] \cdot H_2O$ [A = P (**1a**) or As (**1b**)]. The pH of solution (**A**) was lowered to 4.5 by adding 6 mol dm^{-3} HCl. An aqueous solution (10 cm^3) of $[PPh_4]Cl$ (0.26 g, 0.70 mmol) or $[AsPh_4]Cl$ (0.29 g, 0.70 mmol) was then added with stirring. The precipitated deep green solid in each case was filtered off, washed with water, ethanol, and finally diethyl ether. The green products were crystallised from CH_3OH–diethyl ether and the resulting green microcrystalline solids dried under vacuum over P_4O_{10}. Yields: (**1a**), 0.170 g (75%) and (**1b**), 0.200 g (75%).

$[Re(NO)(OH)_3(L\text{–}L)] \cdot H_2O$ [L–L = phen (**2a**) *or* bipy (**2b**)]. The procedure above was applied using L–L (phen, 0.12 g, 0.70 mmol; bipy, 0.11 g, 0.70 mmol) instead of the counter ions. The chocolate brown precipitate in each case was filtered off and washed with ethanol and diethyl ether. The chocolate brown solid was then extracted with dmf and the brown solid crystallised out by adding diethyl ether. The substance was filtered off, washed as above, and dried in vacuum over P_4O_{10}. Yields: (**2a**) 0.140 g (78%) and (**2b**), 0.130 g (75%).

Preparation of solution (**B**). Solution (**A**) or solid $[APh_4][Re(NO)(OH)_4] \cdot H_2O$ (0.250 g, 0.39 mmol when A = P and 0.260 g, 0.37 mmol when A = As) was boiled with concentrated HCl (40 cm^3) for 30 min. The resulting orange-yellow solution obtained in each case was solution (**B**).

$[APh_4][Re(NO)_2Cl_4] \cdot n\,H_2O$ [A = P (**5a**), n = 1.5, *or* As (**5b**), n = 1]. A cold aqueous solution (10 cm^3) of $[APh_4]Cl$ (0.26 g for A = P or 0.29 g for A = As, both 0.70 mmol) was added to solution (**B**) with stirring. A greenish yellow precipitate separated immediately, which was filtered off, washed with water and ethanol, and dried *in vacuo.* The dry solid was then extracted with $CHCl_3$ (15 cm^3) and the $CHCl_3$ extract was collected leaving behind a residue. The extract on treatment with n-pentane (10 cm^3) gave a dirty pale yellow precipitate which was removed by filtration and the clear greenish solution was slowly evaporated to deposit a light green microcrystalline solid. This was collected by filtration, washed with diethyl ether, and vacuum dried in each case. Yields: (**5a**), 0.090 g (30%) and (**5b**), 0.090 g (30%).

$[\mathrm{APh_4}][\mathrm{Re(NO)Cl_5}]\cdot\mathrm{H_2O}$ [A = P (**3a**) *or* As (**3b**)]. The chloroform-insoluble residue obtained above was dissolved in $\mathrm{CH_3CN}$ (5 $\mathrm{cm^3}$) and the resulting solution deposited orange crystals on treatment with diethyl ether (10 $\mathrm{cm^3}$) in each case. The crystals were collected by filtration, washed with diethyl ether, and vacuum dried. Yields: (**3a**), 0.085 g (30%) and (**3b**), 0.090 g (30%).

$[\mathrm{NBu^n{}_4}][\mathrm{Re(NO)_2Cl_4}]$ (**5c**). A cold aqueous solution (10 $\mathrm{cm^3}$) of $[\mathrm{NBu^n{}_4}]\mathrm{Cl}$ (0.21 g, 0.70 mmol) was added to solution (**B**) whereupon a dark red oily mass separated out. The aqueous layer was decanted off and kept [solution (**C**)]. The red semi-solid was washed twice with water and dried in vacuum over $\mathrm{P_4O_6}$. The dry semi-solid was then rubbed with a glass rod with small portions of n-pentane, several times, to yield a dark red solid. Yield 0.085 g (36%).

$[\mathrm{Re(NO)Cl_4(phen)}]\cdot\mathrm{H_2O}$ (**7a**). Solution (**B**) or (**C**) was treated with an aqueous solution (10 $\mathrm{cm^3}$) of phen (0.12 g, 0.80 mmol) to yield an orange precipitate. It was collected by filtration, washed with water, ethanol, and benzene and dried *in vacuo*. It was recrystallised from dmf–diethyl ether. The yield was 0.065 g (32%) when prepared from (**B**) and 0.040 g (20%) when obtained from (**C**).

$[\mathrm{APh_4}][\mathrm{Re(NO)_2Br_4}]\cdot\mathrm{H_2O}$ [A = P (**6a**) *or* As (**6b**)]. Solution (**D**) (brown-red) was prepared following the same method for preparing (**B**) using HBr instead of HCl. Starting from (**D**) the same procedure as applied in preparing the corresponding chloro-complex was followed; a red-brown precipitate was obtained. The precipitate was filtered off and processed as for the chloro-complex to yield a red-brown crystalline solid. Yield: (**6a**), 0.100 g (30%) and (**6b**), 0.110 g (30%).

$[\mathrm{APh_4}][\mathrm{Re(NO)Br_5}]\cdot\mathrm{H_2O}$ [A = P (**4a**) *or* As (**4b**)]. Exactly the same procedure for purifying the chloro complex from the chloroform-insoluble residue was followed. Red crystals were obtained in each case. Yields: (**4a**), 0.110 g (30%) and (**4b**), 0.170 g (30%).

$[\mathrm{NBu^n{}_4}][\mathrm{Re(NO)_2Br_4}]$ (**6c**). A cold aqueous solution (10 $\mathrm{cm^3}$) of $[\mathrm{NBu^n{}_4}]\mathrm{Cl}$ (0.21 g, 0.70 mmol) was added to solution (**D**) when a dark red oily mass separated out. The aqueous layer was decanted off and kept [solution (**E**)]. The red semi-solid mass was treated in a similar way to that applied in preparing the corresponding chloro complex to yield a dark red solid. Yield: 0.110 g (36%).

$[\mathrm{Re(NO)Br_4(phen)}]\cdot\mathrm{H_2O}$ (**7b**). Starting from solution (**D**) or (**E**) the same procedure for the corresponding chloro-complex was followed. An orange crystalline solid was obtained. The yield was 0.090 g (32%) when prepared from (**D**) and 0.055 g (20%) from (**E**).

$[\mathrm{PPh_4}]_3[\mathrm{ReI_6}]$. Solution (**A**) or $[\mathrm{PPh_4}][\mathrm{Re(NO)(OH)_4}]\cdot\mathrm{H_2O}$ (0.250 g, 0.39 mmol) was boiled with freshly prepared concentrated (57%) HI (40 $\mathrm{cm^3}$) for 30 min when a deep red solution was obtained. Addition of an aqueous solution of $[\mathrm{PPh_4}]\mathrm{Cl}$ (0.26 g, 0.70 mmol) gave a yellow precipitate which was filtered off, washed with water, ethanol, and carbon tetrachloride, and dried *in vacuo*. The solid was then crystallised from $\mathrm{CH_3CN{-}Et_2O}$, collected by filtration, washed with diethyl ether, and vacuum dried. Yield: 0.110 g (15%) (Found: C, 40.5; H, 2.9; I, 37.3; P, 4.1; $\mathrm{C_{72}H_{60}I_6P_3Re}$ requires C, 41.8; H, 2.9; I, 36.9; P, 4.5%). Λ_M (in acetonitrile, 10^{-3} mol $\mathrm{dm^{-3}}$) = 310 Ω^{-1} $\mathrm{cm^2\ mol^{-1}}$. The compound is diamagnetic.

From the filtrate no pure product could be characterised.

Acknowledgements

This work was kindly supported by the University Grants Committee, New Delhi. We thank the Alexander von Humboldt Foundation (West Germany) for donating the PE 597 infrared spectrophotometer and Professor A. Müller (Bielefeld, West Germany) for far-i.r. spectra (300—150 $\mathrm{cm^{-1}}$). We also thank Professor A. Chakravorty (Indian Association for the Cultivation of Science, Calcutta) for the electrochemistry and e.s.r. spectra and Dr. N. Ray Chaudhuri of the same Institute for the thermoanalytical work.

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Received 3rd *February* 1987; *Paper* 7/185